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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



Applicant's or agent's file reference PSIC064WO	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/16)	
International application No. PCT/EP 03/04242	International filing date (day/month/year) 22.04.2003	Priority date (day/month/year) 25.04.2002
International Patent Classification (IPC) or both national classification and IPC C08G18/12		
Applicant SICPA HOLDING S.A.		

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

 These annexes consist of a total of 4 sheets.

- This report contains indications relating to the following items:
 - ☒ Basis of the opinion
 - ☐ Priority
 - ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - ☐ Lack of unity of invention
 - ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - ☐ Certain documents cited
 - ☐ Certain defects in the international application
 - ☐ Certain observations on the international application

Date of submission of the demand 04.10.2003	Date of completion of this report 12.07.2004
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Scheuer, S Telephone No. +49 89 2399-8321 

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International application No. **PCT/EP 03/04242**

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-15 as originally filed

Claims, Numbers

1-18 received on 16.12.2003 with letter of 15.12.2003

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-18
	No: Claims	
Inventive step (IS)	Yes: Claims	1-18
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-18
	No: Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: EP-A-0604890

D2: WO-A-01/14442

Art.33(2) PCT:

D1 discloses a polyurethane resin which is the reaction product of a high molecular weight polyol such as polyether polyol having a molecular weight of 3000 to 10000 (p.4/39-57), a low molecular weight polyol having a molecular weight of not more than 200 such as aliphatic diols (p.5/8-13), an organic diisocyanate (p.5/18-23), an aliphatic diamine (p.5/24-28) and a reaction terminating agent (p.5/34-35). The polyurethane resin useful as a binder for printing ink for a laminate exhibits excellent adhesiveness for various kinds of plastic films and blocking resistance and excellent adaptability for boiling or retorting treatment.

D2 discloses a polyurethane resin being the reaction product of a diisocyanate with a polymeric diol selected from the group consisting of one or more polyether diols, polyester diols and mixtures thereof, a diamine and optionally an amine or alcohol.

The subject-matter of claims 1 and 13-18 differ from D1 and D2 in that the group of components having isocyanate reactive functional groups and used to prepare the polyurethane resin comprises in particular polyhydroxylated resins selected from the group consisting of hard ketonic resins, ketonic resins, unsaturated styrene-free polyester resins, acrylic-styrene copolymers, acrylic polyols, rosin derivatives and terpene-phenolic resins

The subject-matter of claims 1-18 is therefore new (Article 33(2) PCT).

Art.33(3) PCT:

The document **D1** is regarded as being the closest prior art to the subject-matter of claims 1 and 13-18. The problem to be solved by the present invention may be regarded as to provide polyurethane resins applicable as film forming binders in coating compositions showing a good initial adhesiveness and a good compatibility with alcohols as well as good heat resistance and especially showing good adhesiveness on

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specific substrates and being harder than common polyurethane resins.

The solution to this problem proposed in claim 1 of the present application is considered as involving an inventive step (Article 33(3) PCT) because the use of specific polyhydroxylated resins as disclosed in claim 1 to prepare polyurethane resin is nowhere disclosed or suggested in D1, and a film forming binder can be obtained particularly suitable for obtaining layers which are not damaged during storing and further processing of the substrate-film and during finishing of the laminate.

Claims 13-18 are dependent on claim 1 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

Art.33(4) PCT:

The subject-matter of the present application is considered to meet the requirements of Art.33(4) PCT.

Amended Claims

1. A polyurethane resin being the reaction product of at least one diisocyanate and a group of components having isocyanate reactive functional groups, said group of components comprising:
 - a) a first group of one or more polyether polyols each having an average molecular weight in the range of between 400 to 12000 g/mol,
 - b) a second group of one or more polyhydroxylated resins selected from the group consisting of hard ketonic resins, ketonic resins, unsaturated styrene-free polyester resins having a hydroxyl number below 100 g KOH/g, acrylic-styrene copolymers, acrylic polyols, rosin derivatives and terpene-phenolic resins,
 - c) optionally a third group of one or more polyols each having an average molecular weight of equal or less than 800 g/mol and which are selected from the group consisting of monomeric diols, dihydroxy polyether polyols, polyester polyols, and
 - d) at least one amine and a reaction terminating agent,wherein the ratio of the equivalent weights of the diisocyanate to the components having isocyanate reactive functional groups is selected such that essentially all of the isocyanate groups of the diisocyanate are present as the reaction product with one of said isocyanate reactive functional groups.
2. A polyurethane resin according to claim 1 wherein the ratio of the equivalent weights of the diisocyanate to the entirety of the polyether polyols of the first group, of the polyhydroxylated resins of the second group and of the polyols of the third group is in a range of 3.6:1 to 1:1, preferably 1.5:1.
3. A polyurethane resin according to any one of the claims 1 or 2, wherein the ratio of the equivalent weights of the diisocyanate to the components having isocyanate reactive functional groups is preferably in a range of between 0.8:1 to 1.2:1, more preferably of between 0.95:1 to 1.2:1, and even more preferably of between 1:1 to 1.1:1.

4. A polyurethane resin according to any one of the claims 1 to 3, wherein the ratio of the equivalent weights of the diisocyanate to the amines is in a range of 2:1 to 6:1, preferably in a range of between 3:1 to 6:1, and more preferably in a range of between 3:1 to 5:1.
5. A polyurethane resin according to any one of the claim 1 to 4, wherein the polyether polyols of the first group have an average molecular weight in the range of from 2000 to 6000g/mol.
6. A polyurethane resin according to claim 5, wherein the polyether polyols of the first group are selected from the group consisting of dihydroxy and trihydroxy polyether polyols.
7. A polyurethane resin according to claim 6, wherein the dihydroxy polyether polyol is selected from the group consisting of polyoxyalkylene glycol, preferably a polypropyleneglycol or a polytetrahydrofurane, and a caprolactone based polyether.
8. A polyurethane resin according to any one of the claim 1 to 7, wherein the ketonic resins are polyketonic resins, for example aldehyde-ketone resins, cyclohexanone condensation products having preferably a hydroxyl number of 100-200 KOH/g, or condensation products of an aliphatic ketone with formaldehyde having preferably a hydroxyl number below 100 KOH/g.
9. A polyurethane resin according to any one of the claim 1 to 7, wherein the acrylic-styrene copolymers are hydroxy-functional copolymers having preferably a hydroxyl number between 50 and 150 KOH/g.
10. A polyurethane resin according to any one of the claim 1 to 7, wherein the acrylic polyols are resinous polyols having a hydroxyl number between 100 and 200 KOH/g.

11. A polyurethane resin according to any one of the claim 1 to 7, wherein the terpene-phenolic resins have a hydroxyl number between 100 and 200 KOH/g.
12. A polyurethane resin according to any one of the claims 1 to 11, wherein the amine is a diamine, preferably selected from the group consisting of isophoronediamine, m-xylene, 1,3 bis (aminoethyl) cyclohexane.
13. Process for preparing a polyurethane resin according to any one of claims 1 to 12, said process comprising the steps of:
 - a) first reacting a mixture comprising: a first group of one or more polyether polyols each having an average molecular weight in the range of between 400 to 12000 g/mol, a second group of one or more polyhydroxylated resins selected from the group consisting of hard ketonic resins, ketonic resins, unsaturated styrene-free polyester resins having a hydroxyl number below 100 g KOH/g, acrylic-styrene copolymers, acrylic polyols, rosin derivatives and terpene-phenolic resins, and optionally a third group of one or more polyols each having an average molecular weight of equal or less than 800 g/mol and which are selected from the group consisting of monomeric diols, dihydroxy polyether polyols, polyester polyols, with at least one diisocyanate to an isocyanate terminated prepolymer, the ratio of the equivalent weights of the diisocyanate to the entirety of the polyether polyols of the first group, of the polyhydroxylated resins of the second group and of the polyols of the third group is in a range of 3.6 : 1 to 1 : 1, and
 - b) in a second step reacting said isocyanate terminated prepolymer with at least one diamine, and
 - c) in a third step reacting the product obtained according to step b) with a terminating agent to a saturated polyurethane resin.
14. Polyurethane resin, obtainable by the process according to claim 13.
15. A coating composition, preferably printing ink, comprising a solvent and at least one polyurethane resin according to one of the claims 1 to 12 or 14 as film forming binder.

16. Use of a polyurethane resin according to claims 1 to 12 or 14 as at least one film forming binder in printing inks for printing plastic substrates, preferably polyolefinic plastic substrate.
17. Method of producing a laminate carrying a printed layer, said method comprises the steps of
- a) -providing a-coating composition, preferably a printing ink, according to claim 15;
 - b) applying a layer to a first substrate, preferably a plastic foil, by printing said printing ink of step a) in a flexographic and/or gravure printing process;
 - c) removing said solvent from said layer thereby drying and/or curing said layer obtained in step b),
 - d) applying an adhesive to the dried and/or cured layer obtained in step c) and producing the laminate by applying at least a second substrate, preferably a plastic foil, on the adhesive.
18. Laminate produced by the method of claim 17.